THE ACID-BASE CATALYSIS OF HYDROGEN

ISOTOPE EXCHANGE REACTIONS

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ISOTOPE EXCHANGE REACTIONS

/Following is the translation of an article
by A. I. Shatenshteyn, Ye. N. Zvyagintseva,
Ye. A. Yakoleva, Ye. A. Izrailevich, Ya. M.
Varshavskiy, M. G. Lozhkina, and A. V.
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I. INTRODUCTION

When heavy water became available it was utilized for
the study of acid-base catalysis. Comparison of the chemical
reaction velocities, catalized by acids and bases in ordinary
and heavy water, disclosed deceleration as well as accelera-
tion of reactions in heavy water. The sign of the isotope
effect indicates which stage of speed determines the
kinetics reaction. With acid catalysis, such stages are:
joining of proton (deuteron) to the reacting substance —
substraction and disintegration of the complex /1-5/.

Acids and bases catalyze the hydrogen isotope ex-
change reactions in substances dissolved in heavy water.
There are many observations concerning homogeneous catalysis
of the hydrogen exchange reactions. However, quantitative
measurements of their velocity and activating energy are
comparatively scarce /1-3/.

The area of hydrogen exchange reactions broadened
when instead of heavy water other compounds of deuterium
and new catalyzers became available. Ingold and coworkers
/6/ were first in accomplishing isotope exchange of
hydrogen D_2SO_4 and some saturated hydrocarbons. The study
of the latter was offered by American authors (Burwell and
Gordon, Beeck and Stevenson /7/) and by D. N. Kursanov
jointly with V. N. Setkina /8/. Polaneyi with coworkers
and Klit and Langseth /9/ discovered that the hydrogen
exchange between C_6H_6 and DCl in the presence of $AlCl_3$
occurs rapidly even at room temperature. Kharash with
coworkers /10/ used C_2H_5OD for hydrogen exchange because
organic substances dissolve better in it than in water.
Brown /11/ accomplished some exchange reactions with

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CH_3CO_2D by means of sulfuric acid catalysis.

While studying hydrogen exchange in nonwater solutions, our laboratory at first used very strong bases and acids (for instance, ND_3, $ND_3 + ND_3^-$, DBr, $DBr + AlBr_3$, DF, $DF + BF_3$). We calculated that this would result in deeper understanding of the type and of the rules governing these reactions and make clearer their mechanism; we also hoped to obtain new information on the reaction ability and acidity-basicity of organic compounds in connection with their structure and physical and chemical properties of the reacting medium. The results of the laboratory works were discussed in reviewed articles devoted to the mechanism of the hydrogen exchange in solutions /12/, reaction ability of organic substances /13/ and acidity-basicity of hydrocarbons /14/. This report on acid-basis catalysis of the hydrogen exchange reactions is a generalization of the results of mostly unpublished works conducted by Ye. N. Zvyagintseva, Ye. A. Yakovleva, Ye. A. Israilevich, Ya. M. Varshavskiy, M. G. Lozhkina, and A. V. Vedeneyev.[*]

2. RULES OF ACID-BASIS CATALYSIS

While discussing acid-basis catalysis of hydrogen exchange reactions, we must first of all consider rules established for homogeneous catalysis in solutions /2/. Such is the well-known equation of Brensted: the reaction velocity constant is proportional to the constant of the catalyzer dissociation in a degree less than one, $k = gK^a$. Similar relationships discribe the effect of changing force of the substratum as protolite at the assigned catalizer /15, 2/.

Upon catalysis by concentrated solutions of acids an equation of Hammett /16/ is usually observed: the logarithms of the reaction velocity constant are proportional to the function of the acidity of the acid Ho. The function Ho expresses the degree of ease of the proton transition to the uncharged molecule of the basis.

$$H_0 = -\frac{\lg K_B \cdot c_{BH^+}}{c_B},$$

where Kb is a reaction equilibrium constant $BH^+ \rightleftarrows B + H^+$,

$$K_B = \frac{a_{H^+} \cdot a_B}{a_{BH^+}}.$$

Hine /17/ recorded the applicability of rules of general catalysis by bases to isotope hydrogen exchange between chloroform and water.

According to Beeck and Stevenson /18/, the Hammett rule is justified upon isotope exchange of hydrogen between isobutane and sulfuric acid, and Gold, Long, and Satchell /19/ substantiated it upon the exchange of hydrogen between anthracene and sulfuric acid of various concentrations, and also upon catalysis of sulfuric, hydrochloric, and phosphorus acids of the hydrogen exchange in benzene, p-nitrophene and p-cresol.

In cases when we deal with solvents which are strong protolithic agents, the noted relationships of Brønsted is impossible to authenticate quantitatively in view of the absence of a dissociation constant for such systems. They can be conformed qualitatively. For instance, there is a parallelism between the velocity of the hydrogen exchange reactions, catalized by a solution of potassium amide in liquid deuteroammonium, and the relative acidity of the hydrocarbons, expressed in a form of a conditional dissociation constant, determined by Conant and Wheland according to the degree of equilibrium displacement with participation of alkali-organic compounds /20, 21, 14/. The relative velocity of hydrogen exchange between hydrocarbons and the acid-solvents is comparable to the degree of basicity of the hydrocarbons, established by other means /14/.

For such solvents as liquid HBr and HF, and also solutions of $AlBr_3$ in liquid HBr and of BF_3 in liquid HF, the function of acidity was not determined and the authentication of the Hammett equation is as yet impossible.

The methods of comparison of alkalinity of strong basis are almost undeveloped. Upon catalysis with a base, the relationship of the base to proton (expressed in large calories) has importance, but the existing data is scarce; for instance, for the substances of interest to us, the following values were found:

$$NH_2^- \text{ (410)}, \quad OH^- \text{ (385)}, \quad NH_3 \text{ (214)}, \quad H_2O \text{ (180)}.$$
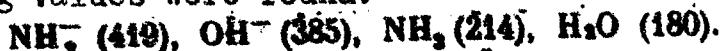
For the noted reasons, it is necessary at this time to limit ourselves to qualitative discussion of results obtained with reference to homogenous catalysis of the exchange reactions in the mentioned solvents, though the results by themselves in the majority of cases are of a qualitative character.

3. PROPERTIES OF SOLVENTS

Table 1 contains protophilic, amphoteric, and protogenic solvents with which our laboratory conducted reactions of hydrogen exchange; it also contains the dielectric

constants (DP) and the dipole moments. The strongest base is placed at the top of the table and the strongest acid at the bottom of the table. In view of the lack of a practically useful single scale of acidity-basicity, it was necessary for us to be guided by constants of dissociation in water solutions ($pK_{H_2O} = -lgK_{H_2O}$). As to application to substances themselves, this is not only conditional but also rather erroneous.

Of the amphoteric solvents, the table presents water and ethyl alcohol. Judging by some works /22, 23/, their acid-base properties are close but the ethyl alcohol is more acid than water.

Dielectric constants and dipole moments of studied solvents.

Solvent	pK_{H_2O}	Dielectric constant.	$\mu \cdot 10^{18}$
$NH_2CH_2CH_2NH_2$	4,0	14	1,94
$NH_2CH_2CH_2OH$	4,6	38	2,27
NH_3	4,7	16	1,46
NH_2NH_2	5,5	52	1,84
H_2O	—	80	1,84
C_2H_5OH	—	25	1,70
CH_3COOH	4,7	6	1,73
HF	3,2	80	1,91
HBr	— 9	4	0,79
HI	—11	(3)	0,38

The DP role of the solvents in acid-base equilibrium and in catalysis is foreseen by Brensted theory, in connection with the fact that this theory treats the acid-base interaction as a process of proton transition, calling in the case of electroneutral molecules for the formation of ions. It is natural that the latter must depend on the DP medium. However, it is now immediately clear that the Brensted theory expresses a limiting condition of those processes which accompany acid-base interaction. Many facts /24, 25, 14) allow us to conclude that the reactions between acids and bases proceed through a stage of polarized complexes, in which the reagents are connected by means of a hydrogen

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bridge. Depending on conditions (among them the DP of the solvent) the reaction may stop at this stage or be completed by transition of the proton to the base and to formation of ions.

Table I also presents dipole moments of molecule solvents, inasmuch as their polarity must favor the emergence of noted complexes due to dipole interaction. In addition, the dipole solvent participate in solvation at the expense of energy which facilitates the rupture of molecules on ions. Participation of a solvent in the exchange reactions is made sharply apparent in the case of catalyses by ions (for example, by ions of $C_2H_5O^-$) which are devoid of deuterium.

When we deal with various solvents and catalyzers it is important to know how the velocity of isotope exchange changes during the transition from one solvent to another in the absence or with the addition of catalyzer. It is desirable to compare the activity of one and the same catalyzer in various solvents. The comparisons are handicaped by the fact that the hydrogen C-H -bands usually very slowly exchange with amphoteric solutions whereas the exchange velocity with basic and acid solvents in presence of catalyzer occasionally is immensely great.

4. COMPARISON OF DEUTEROEXCHANGE WITH AMPHOTERIC AND PROTOPHILIC SOLVENTS

In works of Ye. N. Zvyagintseva there is an attempt to estimate to what extent the velocity of the hydrogen exchange in the substances (in indene, acetophenone, methylnaphthyl ketone) varies with amphoteric and protophilic solvents (deuteroalcohol or deuteroammonium) and, as was said, in both solvents (Table 2). Hydrogen exchange with alcohol even at 120-150° proceeds slower than with ammonia at 0°. Knowing approximately the activating energy of the isotope exchange in ammonium solution (for indene 12 kcal., for acetophenone 10 kcal.), we find that at identical temperatures the constants of the reaction velocities in both solvents differ by 4 to 6 orders. Such is the consequence of the great protophilic property of ammonia in comparison with alcohol.

We supposed that the ratio of the reaction velocity may change if the protolithic function of the substratum in each of the solvents is different. For verification we turned to the methylated nitrous heterocyclics- quinaldine and picoline, inasmuch as in alcohol solvent they are bases, and in ammonium - weak acids /26, 27/.

Experiments of Ye. N. Zvyagintseva indicated that hydrogen in methyl groups of quinaldine and α picoline exchanges with alcohol even faster than with ammonia.

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Table 2

elocity of the hydrogen exchange of some organic substances
with deuteroalcohol and deuteroammonia.

Вещество	°C	pk* (I) C₂H₅OD	pk (II) C₂H₅OD+C₂H₅O⁻ (1 н.)	pk (III) ND₃	pk III—II	pk I—III
2 Инден	150	6	—	(0)	—	(6)
»	0	—	3,4	8,7	0,8	—
3 Ацетофенон	120	7	—	(2,5)	—	4,5
»	0	—	4,5	5	0,5	—
4 Метилнафтилкетон	120	6	—	—	—	—
»	0	—	—	5	—	—
5 Флуорен	25	—	3,4	3,7	0,8	—
»	180	7	—	—	—	—
6 Хинальдин	120	6,2	(2,7)	7,2	(4,5)	—1
7 Пиколин	120	7,4	4,5	9,4	4	—1

* pk = —lgk (сек.⁻¹).

-substance; 2-indene; 3-acetophenone; 4-methylnaphthyl
stone; 5- fluorene; 6-quinaldine; 7-picoline.

nerefore, the relation of hydrogen velocities in two sol-
ents depends not only on protolithic properties of these
olvents but also on the structural peculiarities of the
ubstratum.

To what extent does an addition of alcoholate
nange the velocity of the exchange in alcohol solutions?
rom Table 2 it is apparent that upon catalysis by In.
lcoholate solution the exchange reactions proceed faster
han with ammonia. This is not surprising, because the
ffinity of the ethoxy-ion to a proton in kilocalories is
50 times greater than the affinity of the ammonia molecule.
ndirect comparison indicates that in the first group of
ubstances (indene, acetophenone), in the presence of the
$_2H_5O$ ion, hydrogen exchanges by 4-6 times, and in groups
f heterocycles (quinaldine, picoline) by 3 times, faster
han in pure alcohol.

In experiments with alcohol solution of alcoholate
1 n.) for the first group of substances k is greater by
.3-0.5 times than in experiments with ammonia, and in
eterocycles the exchange proceeds with a speed four times.
t is probable that this occurance-analogous with non-iden-
ical change of dissociation constants of variously struc-
ured acids - is observed upon a change of the solvent.
umerous examples of similar departure from Brensted theory

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are described in works of N. A. Izmaylov /25/. Cases are known when the corresponding divergences between the constants of the acid dissociation reach up to an order of 6. The noted deviation from Brønsted theory was also stated by M. I. Kobachnik /28/ upon the occasion of examining regulations of tautomeric conversions.

Unexpected was the acid catalysis of the hydrogen exchange in indene by alcohol solution of DCl (at concentration of acid solution In. $k = 1.10^{-5}$ ane without the catalyzer $k = 10^{-6}$, 150°). Koizumi /29/ failed to observe the acceleration of the exchange with heavy water in the presence of DCl. Verification indicated that the hydrogen in the methyl group does not participate in the exchange reaction, catalyzed by acid: two atoms of deuterium, which were introduced into the molecule of indene upon catalysis with alcoholates in deuteroalcohol were unaffected after heating the substance with HCl solution in ordinary alcohol. In quinaldine, however, dissolved in deuteroalcohol, the acid and the base catalyze the exchange of the same atoms of hydrogen (methyl group), and at the same time specifically those atoms which exchange with deuteroammonium. This was substantiated by appropriate experiments.

A solution of KND_2 in ND_3 catalyzes the hydrogen exchange many times greater than the solution of alcoholate in alcohol and this is in conformity with greater proton affinity of ND_2 and ND_3 in comparison with $C_2H_5O^-$ and C_2H_5OD. Let us illustrate this by an example of Ye. N. Zvyagintseva's experiments with quinaldine. As is known, the reactions of hydrogen exchange with C_2H_5OD and ND_3 proceed with closely identical velocity (pk=6.2 and 7.2) at 120°. Upon addition of a base to both solvents the exchange velocities are equal (pk = 4) but in entirely dissimilar conditions: 120° for 0.1 n. solution of alcoholate in alcohol and -30° for 0.02 n. solution of amide in ammonium. The factual concentration of amide ions is even much smaller, because this ion is neutralized by quinaldine according to the equation:

$$C_9H_6NCH_3 + ND_2^- \rightleftarrows C_9H_6NCH_2^- + ND_2H.$$
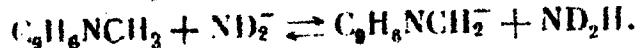
Let us cite another example, where the substance (naphthalene) is such a weak acid that its neutralization of the amide can be neglected. According to measurements by Ye. A. Izrailevich /30/, after heating a solution of naphthalene in liquid ND with deuterium concentrate close to 100% for the duration of 100 hrs at 120° the water of combustion of naphthalene contained less than 0.05 atom. % deuterium. Therefore, $k_{128} < 10^{-9}$ sec^{-1}. Upon

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catalyzing with 0.01 n. of KND_2 the velocity constant is expressed as follows:

$$k = 10^7 \cdot e^{-11900/1.98T}.$$

Allowing that the velocity constant is proportional to the catalyzer concentration, which is not exactly accurate, we find for In. solution $KND_2K=10^1$. Therefore KND_2 speeds up the reaction by at least 10 orders.

In consequence of very high catalytic action of potassium amide, the measurement of the exchange velocity can be achieved only in a comparatively narrow interval of concentration. With increase of the amide concentration from 0.01 to 0.43 n., the hydrogen exchange velocity in benzene (Table 3) increases only 23 times. It is proportional to amide concentration only in the area of low concentrations /30/:

Table 3

Relationship between the hydrogen exchange velocity in benzene and the concentration of deutero-treated potassium amide.*

KND, (n.)	0,01	0,014	0,021	0,059	0,19	0,43
c/c_1	1	1,4	2,1	5,9	19	43
k/k_1	1	1,8	2,0	4,1	9,5	23

* $c_1 = 0,01$ n. $k_1 = 4,4 \cdot 10^{-5}$ сек.$^{-1}$ при 25°.

It appears that the lagging of K with increase of concentration is connected with considerable inter-ion interaction because of low DP (Diss. constant) of liquid ammonium and is due to formation of ion-pairs between ND_2^- and K^+. A similar concentration effect was noted earlier upon study of acid catalysis reactions of ammonolis ammonium (see /31/, page 284).

A solution of KNO_2 in ND_3 so strongly catalyzes reactions of hydrogen exchange that Ye. A. Izrailevich accomplished partial hydrogen exchange in saturated hydrocarbons (Table 4). In truth, the experiments were continued at high temperature (110-120°) for hundreds of hours.

**Experiments were conducted in ampullas of non-rusting steel. Therefore a catalytic effect of the container walls is not excluded. However, control experiment with methylcyclohexane, conducted in glass ampullas (with counter-pressure), marked with an asterisk, indicate that the isotope hydrogen exchange in saturated hydrocarbon proceeds upon

but the exchange was sufficiently measurable; 18% deuterium was introduced into the substance. In Table 4 the following designations are used:

τ -duration of experiment in hrs.

CKN_2-amide concentration (n.)

c_p-concentration of deuterium in solvent.

c_b-concentration of deuterium in the water of ignited substances (atom. %).

n-number of hydrogen atoms changed into deuterium.

There is a noticeable drop in the degree of the exchange with the increase of the catalyzer up to 8n. This observation requires additional verification.

Table 4

Hydrogen exchange catalyzed by potassium amide in saturated hydrocarbons.

1 Вещество	2 τ, часы	c_{KND_2}	c_p	$c_в$	n
3 Гексан	1300	3	10,5	1,8	2,7
4 Гептан	170	0,8	95	13,1	2,1
»	400	8	95	3,3	0,5
»	500	1	95	17,6	3,0
»	1300	3	10,5	2,1	3,5
5 Декалин	180	0,8	95	3,5	1,0
»	420	8	95	0,4	0,1
»	1300	3	10,5	1,6	1,7
6 Циклогексан	180	0,8	95	5,8	0,7
7 Циклопентан	1300	3	10,5	3,3	3,4
8 Метилциклогексан	206	1	50	3,75	1,1
»	500 *	1	50	7,45	2,0

*see reference of preceding page.
1-substance; 2-hours; 3-hexane; 4-heptane; 5- decalin; 6-cyclohexane; 7-cyclopentane; 8-methylcyclohexane.

5. COMPARISON OF VELOCITIES OF DEUTEROEXCHANGE WITH AMPHOTERIC AND PROTOGENIC SOLVENTS.

We shall try to estimate to what extent the exchange reaction is speeded up if instead of water we select various acid solvents and also use catalyzers. According to Small

catalysis with potassium amide and in the absence of metal.

and Wolfden /32/, the heating of a phenol solution in heavy water at 100° causes exchange of two atoms of hydrogen of the aromatic ring after 400 hours; that is, taking into account three atoms of hydrogen. According to Koizumi /33/, in a 0.5 n solution of hydrochloric acid at 100° two atoms of hydrogen exchange every two hours ($k = 10^{-5}$ sec.$^{-1}$). A. V. Vedeneyev /34/ demonstrated that with liquid deuterium bromide, three atoms of hydrogen exchange immeasurably fast even at room temperature. Just as fast goes the reaction between DBr and anisole /34/ but, judging by Brown /11/ measurements, with icecold (glacial) acetic acid anisole does not exchange hydrogen upon heating to 90° for two days. Addition of sulfuric acid (~ 0.1 n. solution in glacial acetic acid) causes under the same conditions an exchange of more than two atoms of hydrogen /11/ (Table 5).

We shall conditionally accept for the reaction of the hydrogen exchange between C_6H_5OH and D_2O $Q = 30$ kcal. and assume that the constant of the velocity exchange between C_6H_5OH and DBr is $k \leqslant 5.10^{-3}$ sec.$^{-1}$. In this case, the velocity reactions is the two mentioned solvents differ by at least 6 to 8 orders.

Hydrogen exchange with liquid deuterium bromide is strongly catalyzed by aluminum bromide. At concentration $\sim 10^{-5}$ mole $AlBr_3$ on 1000 g. DBr the hydrogen of benzene exchanges immeasurably fast at room temperature and very fast at low temperature: during the time of cooling of the solution and evaporation of the solvent (5-7 min.) there is an equilibrium distribution of deuterium, corresponding to temperature -50° -70° /35, 36/. In absence of a catalyzer, the hydrogen in benzene exchanges with liquid DBr exceedingly slow: $k = 5.10^{-8}$ sec. $^{-1}$ at 20° /37/. Therefore, though the estimates appear to be very roughly approximate, it is clear that the hydrogen exchange velocities in organic substances with D_2O and $AlBr_3$ in liquid DBr differ by no less than 20 orders. Catalysis by aluminum bromide is explained by

reaction $\qquad S + D\bar{B}r + AlBr_3 \rightleftarrows SD^+ + AlBr_4^-,$ $\qquad$ where $S =$
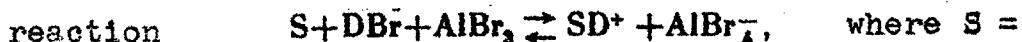
subtratum. In this reaction no free ions are formed.

As a result of exceedingly high catalytic activity of aluminum bromide solution in liquid hydrogen bromide, there appeared to be a possibility of the occurrence of hydrogen exchange even in alicyclic hydrocarbons. Hydrogen exchange in cyclohexane was noted by Ya. M. Varshavskiy and S. E. Vaisberg /38, 39/; and K. I. Zhdanova, V. P. Kalinachenko and L. N. Vinogradov /35/ measured its velocity approximately. At $c_{AlBr_3} = 10^{-2}$ mole/1000 DBr $k \sim 10^{16}$ sec^{-1}.

The velocity exchange constant of the reaction is approximately proportional to the concentration of $AlBr_3$, hydrocarbons

Table 5

1 Вещество	2 Растворитель	3 Катализатор	t, °C	τ, часы	n
Фенол 5	D_2O	—	100	400	2
»	»	HCl (0,5 н.)	100	2	2
»	DBr	—	20	<0,2	3
»	»	—	20	72	3
»	DF	—	20	<0,1	3,3
»	»	—	25	1	4,5
Анизол 6	CH_3CO_2D	—	90	48	0
»	»	D_2SO_4 (0,1 н.)	90	47	2,4
»	DBr	—	20	<0,2	3
»	DF	—	20	<0,05	3,5
»	»	—	25	1	4,8
Дифениловый эфир 7	DBr	—	20	<0,2	6
»	»	»	20	150	6
»	»	DF	20	<0,1	7
»	»	»	25	3	10

1-substance; 2-solvent; 3-catalyzer; 4-hours; 5- phenol; 6-anisole; 7-diphenyl ether.

with a tertiary atom of carbon exchange hydrogen with liquid DF in absence of catalyzer (Table 6). The reaction velocity increases upon addition of BF_3, which, in liquid

deuterium fluoride, is an acidic catalyzer because it displaces the equilibrium of ionization of the solvent by adding an ion of fluorine: $S + DF + BF_3 \rightleftarrows SD^+ + BF_4^-$ *.

Complex formation manifests itself by an increase of solubility of many substances, in coloring of the solutions.

Upon catalysis with BF_3 (0.4 moli.1000 g DF) there occurs an exchange even in a saturated hydrocarbon not possessing tertial atom of carbon and nonisometric (cyclopentane) according to the available data. Therefore, in order to achieve hydrogen exchange between a saturated hydrocarbon and an acid, the presence of tertial carbon

*In liquid DF ionization occurs much easier than in DBr, but the free ions, probably, do not form in all cases.

atom and the presence of an oxidizer are not obligatory, but the acid catalysis is of importance.

Experiments were conducted by shaking in view of the poor solubility of the mentioned substances in liquid DF.

Table 6

Hydrogen exchange of some saturated hydrocarbons with liquid deuterium fluoride in the presence of and in the absence of a catalyzer (BF_3).

1 Вещество	2 т, часы	3 степень обмена (%)
4 Циклогексан	2000	5
5 » +BF₃	200	100
Метилциклогексан	350	80
6 » +BF₃	15	80
Декалин	770	50
7 » +BF₃	7	80
Циклопентан +BF₃	24	70

1-substance; 2-hours; 3-degree of exchange (%); 4-cyclohexane; 5-methylcyclohexane; 6-decalin; 7-cyclopentane.

The comparisons presented in this report for reaction velocities of hydrogen exchange are extremely sketchy but they nevertheless give a descriptive notion of how much broader becomes the entire area of base-acid catalysis of of hydrogen exchange when protophilic and protogenic solvents can be used instead of amphoteric.

6. EFFECT OF DP AND POLARITY OF SOLVENT MOLECULES ON DEUTEROEXCHANGE.

Above we were engaged in a comparison of exchange reactions velocities in amphoteric solvents. On the basis of work by Ye. A. Yakovleva it is possible to say something about the indirect hydrogen exchange in various protophilic solvents - liquid deuteroammonia, anhydrous deutero-hydrazine, and anhydrous deutero-ethylene-diamine. The results of experiments (pk) with fluorene, tri-phenyl-methane, quinaldine and di-phenyl-methane are presented in Table 7, from which it is clear that the velocity of exchange reactions with N_2D_4 and $ND_2CH_2CH_2ND_2$ are greater by 1-1.5 orders than with ND_3. The exchange with hydrozine proceeds faster than with ammonia despite the fact that tri-

Table 7

Values pk at hydrogen exchange of some organic substances
in various protophilic solvents.

| | | 2 Растворитель | | |
Вещество	°C	ND₃	ND₂CH₂CH₂ND₂	N₂D₄
3 Флуорен	25	3,7	2,6	—
4 Трифенилметан	120	6,7	5,7	(5,7)
5 Хинальдин	120	7,2	6,9	—
6 Дифенилметан	120	8,2	7,0	(6,7)

phenyl-methane and diphenyl-methane-soluble in liquid am-
monia are poorly soluble in hydrozine and the reaction pro-
ceeds in a heterogenous system (the pk values are placed in
parentheses).

Let us turn to Table 1, characterizing the proper-
ties of solvents.

The dielectric constants of liquid ammonia and ethyl-
diamine are almost identical, but the polarity of the
second solvent molecule is greater and - if we judge by the
values of its dissociation constant in water - it is a
stronger base. It is probable that this is the reason for
its faster exchange compared with ammonia.

Hydrazine is a weaker base than ammonia but its
molecule is more polar and its DP is more than three times
greater /52 and 16/. We are inclined to think that this
fact is responsible for the speedier exchange with hydra-
zine and this is also noticed in experiments with sodium
acetate.*

As to the effect on the velocity of the hydrogen
exchange of DP and the polarity of the solvent molecules,
all that was successfully demonstrated by a comparison of
kinetics exchange in two acid solvents - liquid hydrogen
bromide and liquid hydrogen fluoride.

Ya. M. Varshavskiy and M. G. Lozhkina /41, 40/
measured the velocity of the hydrogen exchange reactions
between benzine and liquid DF. The velocity appeared to
be 4.3 times greater than the velocity with DBr. Sharp
acceleration of exchange with DF was substantiated by
experiments with tatuene, where the same degree of

*Perhaps, the fact that the number of hydrogen atoms in
molecules of the two last solvents is greater than in the
molecule of ammonia (statistical factor) is of some impor-
tance.

exchange (n = 4.8) was reached at 20° correspondingly after 6 and 90,000 min.

An observation of A. V. Vedeneyev and M. G. Lozhkina /34, 40/ is worth noting - the exchange of all atoms of phenol hydrogen and its esters in liquid deuterium fluoride, in contrast to the exchange of deuterium bromide, which is limited only to three hydrogen atoms of the aromatic rings. Therefore, with DF, the exchange proceeds easier than with DBr (see Table 5).

In the series of hydrogen halides, the acid properties increase from fluorine to iodine, and the hydrogen fluoride appears much less acidic than hydrogen bromide (see Table 1), but in the liquid state it has a DP 20 times greater than the DP of bromide (DP = 80 and 4 correspondingly). The DF molecule is more polar than the DBr molecule. These differences, we believe, are connected with the speeding up of the exchange reactions, when the substances are dissolved in DF.

7. EFFECT OF SUBSTRATUM CHARGE AND CATALIZER ON DEUTEROEXCHANGE.

Let us pause to consider the effect of catalyzer and substratum charge on the velocity of the catalytic reactions in relation to DP solvent. This relationship was made apparent and proven experimentally by Bernsted on an example of a reaction-catalyzed by bases-of dissociation of nitro-amide in water (DP = 80), M-cresole (DP = 13) and iso-amyl-alcohol (DP = 5.7) /see 42, 43, 2, 31/.

The relative velocities of dissociation in the named three solvents upon catalysis of the benzoate ion and the molecule of aniline are given in Table 8, from which it is clear that upon catalysis by ion of benzoate the velocity constants increase in the direction from water to m-cre-sole and to iso-amyl-alcohol, because polarization of the substratum molecule in the area of anion increased with decrease of DP of the solvent. On the contrary, upon catalysis by an electro-neutral molecule of aniline, the constants decrease with the same sequence; high DP contributes to proton transition from one electro-neutral molecule to another.

It is entirely natural that an analogous effect must also be observed with reactions of hydrogen exchange and at the same time it is possible to foresee that in the case of alkali-catalysis the negative charge of the substratum will retard the exchange reaction, catalyzed by a base, because it tends to impede the drawing off or breaking away of the proton. The negative charge of the catalyzer interferes with the approach with the similarly charged substratum,

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especially at low DP of the solvent /44, 12/. Upon acid catalysis, the retardation of the reaction will bring about a positive charge in the substratum because it will impede the junction of the deuterium to the substratum, which is a prerequisite to an exchange reaction.

Indeed, from Ye. A. Yakovleva /44/'s work it is apparent that the velocity of the hydrogen exchange in acetate ion with heavy water (DP = 80) and with deutero-ammonia (DP = 16) is almost identical and somewhat less than the velocity exchange in anhydrous deutero-hydrazine (DP = 52). The following values were obtained for pk: 7.2; 7.7; 6.5. There is hardly a difference (Pk$_{120^o}$ = 4.4 and 4.5) in constants of the velocity exchange at identical concentration of ions (1 n.) OD^- in D_2O and ND_2^- in ND_3, catalyzing the

reactions. In order to make clear to what extent the charge of substratum influences the reaction velocity, catalyzed by ions ND_2^-, it is sufficient to recall that in the absence

of a catalyzer hydrogen exchange with liquid deutero-ammonia in the ion of acetate and in the molecule of quinalline proceeds at the same temperature (120°) and with almost the same velocity (pk = 7.7 and 7.2), but in order to achieve close velocity exchange (pk = 4.4 and 4) upon catalysis by potassium amide, it is necessary to conduct the reaction with the ion at 120° and $c_{knd_2} = 1$ n., whereas reaction with the molecule proceeds at -30° and $c_{knd_2} < 0.02$ n.

The retardation of the exchange of reaction catalyzed by anions in the presence of a negatively charged substance is substantiated by A. V. Vedeneyev /34/. At a concentration of potassium amide, equal 0.4 n. and at 50°, the exchange of hydrogen in an ion of phenolate proceeds with a velocity smaller by 3 orders compared to benzene.

The retardation of the exchange reaction catalyzed by acid in the presence of a positive charge of the substratum was substantiated experimentally by comparing velocities of the hydrogen exchange reactions in aromatic hydrocarbons.

Hydrogen in anthracene exchanges with liquid DBr 5-6 times faster than in benzene /37/. Knowing that the reaction velocity of the hydrogen exchange between benzene and DF is greater by 4.3 orders than with DBr, it is natural to expect that the exchange between anthracene and deuterium fluoride would proceed immeasurably fast. However, it appeared /40/ that hydrogen in anthracene exchanges with DF at least by one order slower than the reaction of the hydrogen exchange taking place between benzene and DF.

The presented facts are easily explained if we remember the strong ionization of anthracene dissolved in

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Table 8

Velocity of catalytic dissociation of nitramide in various
solvents.

Катализатор	2. Растворитель		
	H₂O	м-C₆H₄(CH₃)OH	3 изо-C₅H₉OH
	4 ДП-80	4 ДП-13	4 ДП-5,7
C₆H₅COO—	1	28	90
C₆H₅NH₂	1	0,8	0,06

-catalyzer; 2-solvent; 3-iso-C₅H₉OH; 4-DP-.

.iquid HF, which was indicated by Klatt's /45/ measurements
of electroconductivity and boiling temperature of solvents.
a proton (or deuteron) joins a molecule of anthracene almost
exclusively in the meso-position /40/. Therefore, the
exchange of meso-atoms proceeds rapidly and the exchange
of the remaining atoms of hydrogen in ion $(C_{14}H_{10}D)^+$ is
impeded.*

According to Reid /47/, the addition of BF results in
full ionization of anthracene in liquid HF₃. Therefore, in
agreement with the presented treatise, the presence of BF,
not only does not increase but actually decreases the isotope
exchange of hydrogen in anthracene by limiting the exchange
only to two atoms. For example, in a solution containing
BF₃ (0.4 mole/1000 g DF), after 2 hours 2 atoms of hydrogen
are exchanged (meso-atoms), but without BF, during the same
time, an exchange of 9 atoms is achieved, whereas in
benzene with catalyzer after one half hour 5 atoms are
exchanged and in the presence of BF₃ (0.1 mole/1000 g DF)
a complete exchange of hydrogen occurs in less than 2
minutes.

In increase of the number of condensed rings leads
to an increase of strength of the aromatic hydrocarbons as
bases /14/ and to heightening the degree of their ionization
in DF /48/ /45/. Correspondingly (Table 9), the velocity

*M. I. Kabachnik called our attention to the fact that the
condition for this is a retardation of the anthracene
ionization.

Besides electrostatic action of the charge during
the exchange reaction, the change in the distribution
of the electron density in molecule of the substance, which
is caused by ionization, is important.

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of the hydrogen exchange, catalyzed by BF_3, decreases in sequence benzene > naphthalene > anthracene.

Table 9

Velocity of the hydrogen exchange catalyzed by boron-fluoride in benzene, naphthalene and antracene.

1 Вещество	2 Концентрация BF_3 мол./1000 г DF	3 τ, мин.	4 % обмена
5 Бензол	0,1	2	100
6 Нафталин	0,2	6	80
7 Антрацен	0,4	120	20

1-substance; 2-concentration BF_3 mole/1000 g DF; 3- min.; 4- % exchange; 5- benzene; 6-naphthalene; 7-anthracene.

At the same time on dissolving in liquid DBr., - that is, when in view of the low DP of the solvent ionization has no essential value, and in the exchange reaction, there participate electro-neutral molecules of hydrocarbons - the exchange is accelerated with the same sequence: benzene < naphthalene < anthracene /49/. This depends on the fact that the stronger the base the easier is the occurence of deuteron transfer to a molecule of hydrocarbon, which - as was noted above - is the necessary stage of the hydrogen exchange reaction with acid.

Thus one and the same cause - acid-base interaction with aromatic hydrocarbon, having non-equivalent hydrogen atoms - may lead -depending on the conditions of the flow of the reaction - to diametrically opposite consequences: to the reversal of the order of the relative velocity reactions of the hydrogen exchange.

Thus, we are convinced that besides protophilic and protogenic properties of the solvent and the catalyzer, which of course exert great influence during the hydrogen exchange reactions it is necessary to take into account at least the following parameters: structural peculiarities and the charge of the substratum and the catalyzer; and DP of the solvent and the polarity of its molecule. These parameters permit a change of the hydrogen exchange velocity: faster exchange may occur in a solvent less basic or less acid; it is possible to retard the exchange despite greater protophilic or protogenic properties of the reagents. Therefore, a comparison of the velocities of hydrogen exchange reactions, without consideration of other circumstances, may lead to erroneous conclusion as to relative

.cidity or alkalinity of substances. The best confirmation
if this is the fact of reversal of the sequence of the velo-
ilty of the hydrogen exchange of aromatic hydrocarbons,
'egarding which the above story was related.

8. PARTICIPATION OF SOLVENT IN CATALYTIC EXCHANGE

Unquestionably, the exchange reaction is connected with
iroton (or deuteron) transition from substratum to catalyzer
ir from catalyzer to substratum, while a complete transition
.s not obligatory. Undoubtedly, participation of solvent in
the exchange reaction is of importance. This is apparent
from the fact that though the ion $C_2H_5O^-$ is deprived of
leuterium the isotope exchange occurs, and it is clear that
.t is caused expressly by the $C_2H_5O^-$ ion, because otherwise
the latter would not be able to perform the function of
:atalyzer. It follows that the solvent participates in the
'eaction. Therefore, it is of interest to know how, with
the same substractum and catalyzer, the velocity of the reac-
:ion changes with the change of the solvent, its peculiar-
ities, properties, constants. This question is as yet insuf-
'iciently illuminated and its exploitation may result in
introducing new understanding of the exchange mechanism.
[t is necessary, of course, to remember that sometimes
mder the influence of solvent, the catalyzer may change;
for instance, in an excess of alcohol, the hydroxyl-ion
burns into a ethoxy-ion /23/.

Ye. A. Vakovleva and Ye. N. Zvagitseva obtained some
facts relative to hydrogen exchange catalysis in methenyl
group of tri-phenyl-methane by C_2H_5O ion in ethyl alcohol
and ethyline-diamine and by the $NH_2C_2H_4O$ ion in ethyline-
liamine and ethanolamine. It was found that though at a
concentration of $C_2H_5O^-$ in alcohol equal to 1 n. and of
$NH_2C_2H_4O$ in ethanolamine equal to 0.1 n., the constants
of the velocity exchange reactions are equal correspond-
ingly to 3.10^{-5} and 2.10^{-5} sec.$^{-1}$ at 120^0, the same cata-
lyzers dissolved in anhydrous ethylenediamine at concen-
trations less than 0.1 n. lead to complete exchange of the
nethenyl hydrogen of tri-phelyl-methane after 15 min. at
temperature 25^0. The work continues.

9. CATALYTIC ISOMERIZATION OF HYDROCARBONS.

Acid-base catalysis of the hydrogen exchange sometime
is accompanied by catalysis of the hydrocarbon isomerization.
The presence of isomerization is evident through the change

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Table 10

Isomerization examples of hydrocarbons.

1 Вещество	*2* т. кип., °C	n_D^{20}
3	Раствор KNH₂ в жидком NH₃	
4 Пентен-1:		
5 до опыта	29,5	1,3719
6 после опыта	36,0	1,3810
7 Пентен-2 (литер. данные):		
8 транс	37,0	1,3822
9 цис	36,3	1,3790
10 Диаллил:		
5 до опыта	59	1,4040
6 после опыта	82	—
11 Дипропенил (литер. данные) *16*	82	1,4512
	Раствор BF₃ в жидком HF	
12 Метилциклопентан:		
5 до опыта	71,6	1,4097
6 после опыта	77,0	1,4220
13 Циклогексан (литер. данные)	80,7	1,4262
Декалин:		
14 *5* до опыта	191,0	1,4770
6 после опыта	185,5	1,4695
15 Декалин (литер. данные):		
9 цис	193,3	1,4804
8 транс	185,3	1,4701

1-substance; 2- t. boiling C°; 3- solution KNH₂ in liquid NH₃;
4- pentene - 1; 5- before experiment; 6- after experiment;
7- pentene -2(lit.data); 8- trans-; 9-cis-; 10-diallyl;
11-di-propenyl (lit. data); 12-methyl-cyclo-pentane;
13-cyclohexane (lit. data); 14-decalin; 15-dicalin (lit.
data); 16-solution BF₃in liquid HF.

of constants and the appearance of new frequencies in the
substance's spectral oscillations. Table 10 gives some
examples of hydrocarbon isomerizations, catalyzed by solu-
tions of potassium amide in liquid ammonia (N. M. Dykhno,
L. N. Vasileva, see /50/, also /51/) and tri-fluoride boron
in liquid hydroge fluoride (Ya. M. Varshavskiy, M. G.
Lozhkina).
After treatment of cyclohexane with aluminum bromide

in liquid hydrogen bromide, there appears a band with frequency 890 cm.$^{-1}$ in the spectrum of the combined dispersion of the hydrocarbon which is typical for methylcyclopentane /see 35/.

Isomerization of hydrocarbons accompanying reactions of hydrogen exchange in the noted solvents upon action of the named catalyzers is as yet insufficiently studied and the specific mole which is played by it is not clear. For instance, in order to explain how complete hydrogen exchange is achieved in ethylene hydrocarbons with a long chain of carbon atoms and a double bond at the beginning or in alicyclic hydrocarbons with a double bond in side chain, it is necessary to admit that the potassium amide causes migration of the double bond along the chain of the carbon atom and from the side chain to the cycle /50, 52/. It is possible that the hydrogen exchange in cyclohexane with liquid DBr in presence of AlBr$_3$ and with liquid DF at catalysis of BF$_3$ is favored by the equilibrium isomerization in methylcyclohexane. In the nearest future it will be necessary to establish the velocity ratio between the isomerization reactions and the hydrogen exchange.

10. CONCLUSION

In this report, the question of acid-base catalysis of hydrogen exchange reactions was discussed. The very fact of such catalysis speaks first of all of the fact that hydrogen exchange is actually caused by acid-base interaction — a thesis in the foundation of which the Isotope Reactions Laboratory was actively participating. The majoirty of the parameters which influence velocity of hydrogen exchange reactions were visualized on the basis of the existing theory of acid-base equilibrium and catalysis of Bernsted. There parameters were made distinctly apparent in works summarized in the report. Moreover, it is now clear that the Bernsted theory only approximately describes acid-base processes, because the latter do not necessarily amount to simple proton transition. For further development of the theory, an accumulation of new experimental material will be of assistance.

Though in this report, dedicated to catalysis of the hydrogen exchange, little was said relative to the mechanism of the process, it is obvious that this question is impossible to discuss without consideration of the laws of acid-base catalysis of exchange reactions.

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